

Boundary effects on solute transport in finite soil columns

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Abstract. This study investigates the influence of inlet and outlet disturbances and formulated boundary conditions on the estimation of the dispersion coefficient and retardation factor for short soil columns. Unsaturated miscible displacement experiments utilizing a Br⁻ tracer were carried out on undisturbed columns of a fine-textured Ultisol. Solutions were applied using either a fritted plate or an array of dispensing tips that produced droplets at a prescribed flow rate. One and two-layer analytical solutions of the advective-dispersive equation were fitted to effluent concentrations using nonlinear least squares parameter optimization. Comparison of two-layer simulations with experimental data indicated that the analytical solution with a semi-infinite interface boundary best approximated effluent concentrations under the conditions of this study. This solution corresponds to a continuous flux concentration and a macroscopically discontinuous resident concentration at the interface between the soil and porous plates. Parameter estimates were not significantly different with respect to the application method used at the inlet. This may be attributed to a less uniform distribution of solution onto the soil surface by the drip apparatus and/or by the presence of stagnant regions within the inlet reservoir and hence increased dispersion within the inlet platen apparatus. Two-layer simulations indicated that the dispersion coefficient was underestimated by 14-27% when the influence of the inlet and outlet apparatus were not included in the fitted solution of the advective-dispersive equation. In addition, use of one-layer analytical solutions caused the retardation factor to be overestimated by no more than the fractional increase in pore volume imparted by the platen apparatus.

1. Introduction

Studies of solute transport are often limited to the analysis of breakthrough curves over relatively short longitudinal distances. For instance, soil vertical heterogeneity complicates the analysis of transport and a complete description of the mechanisms often requires that each soil horizon be examined separately. In modeling the data obtained, one uses a mechanistic model with appropriate boundary and initial conditions to fit experimental breakthrough curves and quantify model parameters. When dispersivity is large in comparison to the distance from the inlet to the sampling point, the boundary conditions used to formulate the solution to the model can influence the estimates of parameter values. In addition, physical disturbances at the boundaries brought on by the presence of inlet and outlet apparatus or by spatially heterogeneous application rates at the inlet boundary may also influence the results obtained from miscible displacement experiments.

Previous studies which have evaluated the suitability of prescribed boundary conditions to predict measured solute concentrations in carefully controlled column experiments [James and Rubin, 1972; Parker, 1984; Novakowski, 1992b] have addressed the case of saturated flow in artificial, non-

reactive media. Herein we consider reactive solute transport in unsaturated, undisturbed soil columns. Solute transport under these conditions is of major importance in understanding and determining the movement of contaminants in the vadose zone. Unsaturated transport in fine textured media introduces several difficulties in conducting and analyzing column experiments. First, the establishment of unsaturated flow in columns is typically carried out using outlet apparatus that possess poorly mixed reservoirs. Although the volume of the lower reservoir can be minimized by enclosing a fraction collector in a vacuum, this procedure becomes impractical for large diameter columns at modest flow rates. Alternatively, outlet effects can be accounted for in the numerical solution to estimate the amount of dispersion that occurs only in the media [e.g. James and Rubin, 1972]. Secondly, the use of reactive media with a wide range in particle size may introduce a certain degree of local nonequilibrium at high pore water velocities. Parker [1984] has shown that the analytical solution which prescribes a finite boundary at both the inlet and outlet fails to describe measured concentrations in the extreme case where local equilibrium between pore regions is not attained. In this paper, we are principally concerned with slow pore water velocities where such effects are of minor importance and hence the one-region advective-dispersive equation (ADE) should provide a good description to experimental data. The objectives of this study were to evaluate the suitability of several possible solutions of the advective-dispersive equation to describe reactive solute transport in soil columns and to assess the influence of the inlet and outlet apparatus upon effluent concentrations.

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2. Theory

2.1. Boundary Conditions and Analysis of Resulting Solutions

The transport of a linearly exchanging solute through a homogeneous medium under steady state flow conditions is generally described using the advective-dispersive equation

$$R \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (1)$$

where C_r is the resident solution concentration, D is the longitudinal dispersion coefficient, v is the mean pore velocity, R is the retardation factor describing solute sorption, t is time and x is longitudinal distance. Concentrations measured in the effluent, however, are flux averaged rather than fluid volume-averaged resident concentrations. Flux concentration, C_f , is related to resident concentration through the expression [Kreft and Zuber, 1978]

$$C_f(x,t) = C_r(x,t) - \frac{D}{v} \frac{\partial C_r(x,t)}{\partial x} \quad (2)$$

It is easily verified that substitution of (2) into (1) yields the same partial differential equation except that C_r is replaced by C_f .

Certain simplifying assumptions about how concentrations are influenced by boundaries are necessary to reduce the physical complexity of solute transport and obtain analytical solutions to equation (1). Provided that molecular diffusion is negligible and solute transport is purely hydrodynamical, the flux injection of solute into the upper boundary such that solute velocities are proportional to velocities of the particular flow paths causes concentrations to be weighted by the combined flow rates of all flow paths. Under these conditions, it is agreed [Danckwerts, 1953; van Genuchten and Parker, 1984; Parker and van Genuchten, 1984; Barry and Sposito, 1988; Novakowski, 1992a; Novakowski, 1992b] that the correct inlet boundary for flux injections of solute with a concentration of C_0 is

$$\lim_{x \rightarrow 0^+} \left[v C_r - D \frac{\partial C_r}{\partial x} \right] = v C_0 \quad (3)$$

which is a third-type or specified flux boundary condition. Substituting (2) into (3) shows that this inlet boundary condition is equivalently expressed as

$$C_f(0,t) = C_0 \quad (4)$$

Such a boundary would describe, for instance, solution trickled onto the surface at flow rates not exceeding intake rates. Equation (3) is approximately correct for systems in which the surface is in contact with an entrance reservoir provided that the reservoir is perfectly mixed and hydrodynamical dispersion, molecular diffusion, and reverse flow are negligible within the fore-section [van Genuchten and Parker, 1984; Novakowski, 1992b]. Inspection of equation (3) indicates that this third-type, continuous flux boundary condition forces resident concentrations across the inlet at $x = 0$ to be discontinuous for dispersive media.

The specification of the exit boundary condition for a semi-infinite system requires assumptions about the behavior of the resident concentration as x goes to infinity. Intuitively it is

plausible that the change in concentration with respect to distance tends to zero as x goes to infinity [van Genuchten and Parker, 1984] and hence the outlet boundary could be specified as

$$\lim_{x \rightarrow \infty} \frac{\partial C_r(x,t)}{\partial x} = 0 \quad (5)$$

Implicit in the semi-infinite boundary condition above is that exit boundaries do not influence resident concentrations within the column.

The frequently used Danckwerts boundary condition [Danckwerts, 1953] for a finite column of length L assumes that the solute concentration is continuous across the lower boundary (i.e. resident concentrations are equivalent to exit flux concentrations). This assumption results in the exit boundary condition

$$\frac{\partial C_r(L,t)}{\partial x} = 0 \quad (6)$$

where the outlet boundary is at $x = L$.

Each of the above exit boundary conditions, equations (5) and (6), combined with the inlet boundary condition and the initial condition describing a column free of solute

$$C_r(x,0) = 0 \quad (7)$$

yields particular analytical solution for equation (1). Application of the semi-infinite exit boundary condition (5) yields the particular solution [Lapidus and Amundson, 1952]

$$\frac{C_f(x,t)}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{Rx - vt}{2\sqrt{DRt}} \right) + \frac{1}{2} \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left(\frac{Rx + vt}{2\sqrt{DRt}} \right) \quad (8)$$

Application of the finite boundary conditions (6) yields the particular solution [Brenner, 1962; van Genuchten and Parker, 1984]

$$\frac{C_f(x,t)}{C_0} = 1 - \sum_{m=1}^{\infty} \frac{2\beta_m \sin \left(\frac{\beta_m x}{L} \right) \exp \left(\frac{vx}{2D} - \frac{v^2 t}{4DR} - \frac{\beta_m^2 D t}{L^2 R} \right)}{\beta_m^2 + \left(\frac{vL}{2D} \right)^2 + \frac{vL}{D}} \quad (9)$$

where β_m are the positive roots of

$$\beta_m \cot(\beta_m) - \frac{\beta_m^2 D}{vL} + \frac{vL}{4D} = 0 \quad (10)$$

The above solutions for flux concentrations can be transformed to solutions representing resident concentrations using equation (2) [Kreft and Zuber, 1978; van Genuchten and Parker, 1984]. It should be emphasized that the above solutions diverge only for media possessing a large dispersivity relative to the distance from the inlet to the sampling point. This corresponds to Péclet numbers ≤ 10 . For Péclet numbers ≥ 10 , the solutions of (8) and (9) are essentially identical (give absolute differences < 0.01) and hence it makes little difference what solution is employed.

The formulation of exit boundary conditions suitable for the analysis of solute transport in finite domains of highly

dispersive media has been the subject of considerable discussion. *Danckwerts* [1953] reasoned that to avoid the unacceptable conclusion that the solute concentration passes through a maximum or minimum it is necessary to set the resident concentration gradient to zero at the lower boundary. *Parlange and Starr* [1978] conjectured that the lower boundary condition will affect the concentration profile within the entire column. Unlike the inlet where a boundary layer can develop upstream of the column entrance, no boundary layer can develop downstream and equation (6) must hold to insure continuity in concentration at $x = L$ [*Parlange and Starr*, 1978; *Parlange et al.*, 1985]. *Parlange et al.* [1985] recommend that the semi-infinite solution (8) can be used safely only for column Péclet numbers ($Pe = v \cdot L/D$) greater than about four. In contrast, *van Genuchten and Parker* [1985] reasoned that although resident concentrations should certainly be continuous across the exit boundary at the microscopic level, continuity in concentration will not necessarily hold at the macroscopic level when discontinuities in medium properties are imposed. *Parlange et al.* [1992] suggest that the semi-infinite solution (8) should be reliable at Péclet numbers less than 4 only when there is negligible back diffusion at $x = L$. *Van Genuchten and Parker* [1985] rationalized that when dispersion is governed principally by advection, solute distributions inside the finite column should be unaffected by the presence of an outflow boundary imposed on the solution of (1). This is accomplished by considering the column to be part of a semi-infinite domain. *Kreft and Zuber* [1986] pointed out that an implicit outcome of the *Danckwerts* boundary condition (6) is that the boundary is permeable to advection but impermeable to dispersive flow. They added that since it is difficult envision how such a boundary could be realized, equation (6) is a less suitable approximation than conditions used for semi-infinite media.

When dispersion is determined primarily by variations in axial velocity, the concentration near the inlet would not actually show the discontinuity in concentration predicted by equation (3). As a consequence, the reflective boundary at the inlet causes rapid forward diffusion of solute into regions of low concentration [*Nauman and Mallikarjun*, 1983]. The movement of solute particles in and out of the boundaries for a particular analytical solution can be summarized by the quantity termed relative column holdup, which is the fraction of the input solute mass stored within the column as t approaches infinity [*van Genuchten and Parker*, 1984; *Barry and Sposito*, 1988]. Analytical solutions (e.g. equations (8) and (9)) that predict a relative holdup of unity compensate for the enhanced forward dispersion near the inlet by permitting solute particles to reenter or accumulate at the outlet boundary. Although the reentry or accumulation of solute particles at the lower boundary is not physically realistic for advective flow, this phenomenon permits analytical solutions (8) and (9) to exhibit mean residence times unaffected by dispersion. This is unconditionally correct for closed systems [*Danckwerts*, 1953; *Zwietering*, 1959] or equivalently for column experiments where solute particles do not flow upstream and hence cannot reenter the domain once they have exited through the lower boundary.

From the previous discussion it is obvious that a set of

boundary conditions which may be physically unrealistic is necessary to arrive at a proper solution for flux concentrations at the outlet when dispersion is governed principally by variations in axial velocity. This is an unavoidable result of using a parabolic equation to predict physical processes which propagate finitely in time and space. For many real systems, longitudinal dispersion is essentially a mixing process, where velocities do not exceed the maximum velocities of the advective motion. This violation of reality by the ADE requires the formulation of artificial boundary conditions [*Westerterp et al.*, 1995]. Consequently, any attempt to establish which set of boundary conditions are most appropriate must consider the deviations of the analytical solutions from measurements as obtained by column displacement experiments. Similar arguments were presented by *Novakowski* [1992a; 1992b] to demonstrate that the most physically appropriate boundary conditions for the advective dispersive equation could only be resolved by using the results of physical modeling experiments.

The only previous studies which have compared the analytical solutions resulting from differing boundary conditions to measured concentrations are those of *Parker* [1984] and *Novakowski* [1992a, 1992b]. *Parker* [1984] investigated the use of the flux-averaged transformation under steady-state conditions. *Parker* shows that the resident concentrations are best represented by boundary conditions (3) and (5). The finite solution for the lower boundary condition failed to yield correct flux concentrations in the limit as $D \rightarrow \infty$. However, the column Péclet number obtained was small (0.02) and there was limited interaction between large and small pores at high flow rates. The failure of the *Danckwerts* boundary condition to describe experimental data is especially notable for aggregated and fractured media which have high fitted dispersion coefficients as a result of large differences in flux and resident concentrations [*Parker*, 1984]. Under these conditions, however, equation (1) may no longer apply and hence agreement between analytical solutions to (1) and measurements would be difficult to assess with regards to the correct boundary condition. *Novakowski* [1992a, 1992b] carried out an in-depth mathematical and experimental evaluation of boundary conditions for solute transport in columns packed with glass beads and till (with silt and clay removed). Mixing in both the upper and lower reservoir was considered in the formulation of boundary conditions. *Novakowski* [1992b] found that the analytical model in which resident concentrations at the boundaries were macroscopically discontinuous best simulated the measured concentrations in the lower reservoir and within the column.

2.2. Inlet and Outlet Boundary Disturbances

A difficulty sometimes encountered in miscible displacement experiments is that some of the apparent dispersion may be due to the experimental apparatus. Although one-dimensional infiltration is assumed to occur into the upper soil boundary, this may not be strictly true for drip applications and in some cases with porous plates [*Starr and Parlange*, 1977]. Another problem with regard to interpretation of displacement experiments is the effect platen inlet and exit apparatus can

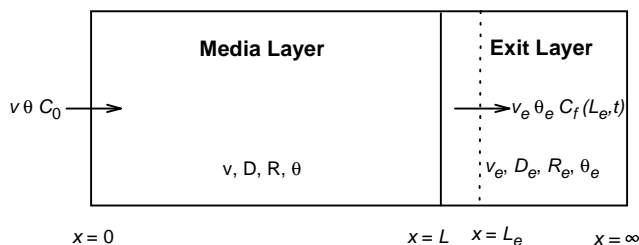


Figure 1. Schematic diagram of transport in a two-layer porous medium and associated coefficients in each layer.

have upon the resulting flux concentrations at the outlet. Often times it may not be possible to sufficiently minimize the fluid volume contained within the exit apparatus. As a consequence, the “true” residence time distribution function is obscured and parameters estimated using the resulting flux concentrations will therefore be in error [James and Rubin, 1972]. Novakowski [1992b] avoided this complication by thoroughly mixing the upper and lower reservoir to establish a known concentration with which to describe the column boundary. Here, we consider platen type inlet and exit apparatus commonly employed in soils investigations of unsaturated flow. Under these conditions, mixing is not complete and the inlet or exit apparatus may behave more like a second layer with distinct transport properties.

Assuming that solute flux concentrations within the media and exit apparatus can be approximated by a two-layered system [James and Rubin, 1972; Leij and van Genuchten, 1995], the effects of the exit apparatus upon parameter estimates for the test media can be indirectly quantified (see Figure 1). Flux continuity requires that $v_e = v \cdot \theta / \theta_e$ where v_e and θ_e are the velocity and volumetric water content respectively in the exit apparatus and θ is the water content of the porous media. If the exit apparatus is non-reactive, $R_e = 1$, then the only remaining unknown is the dispersion coefficient for the exit apparatus, D_e . The analytical solution for resident concentrations in the second layer of a two-layer medium with a first-type inlet boundary (4) and semi-infinite boundaries (5) at the interface and exit have been obtained by Shamir and Harleman [1967] and Leij et al. [1991]. Given a prescribed flux boundary condition $f(L, t)$, it is easily shown that by convolution to obtain the inverse Laplace transform, the solute flux concentration in the second layer with initial condition (7), an inlet boundary (4), and the exit boundary (5) for the second layer yields

$$\frac{C_f(x, t)}{C_0} = \frac{\sqrt{R_e} \cdot (x - L)}{2 \cdot \sqrt{D_e} \pi} \int_0^t f(L, \tau) \cdot \frac{1}{\sqrt{(t - \tau)^3}} \cdot \exp \left[\frac{-(R_e(x - L) - v_e(t - \tau))^2}{4 R_e D_e (t - \tau)} \right] d\tau \quad (11)$$

for $L < x < L_e$ where L_e is the distance from the column inlet to the outlet. Equation (11) implicitly assumes that concentrations in the first layer are not influenced by the exit apparatus and hence flux concentrations at the interface can be applied to the second layer. The boundary condition applied at the

interface corresponds to the analytical solution used to obtain $f(L, t)$. For a semi-infinite boundary at the interface, $f(L, t)$ is described by equation (8) whereas for a Danckwerts-type boundary condition, $f(L, t)$ is given by (9). A mass balance conducted on equation (11) using either inlet condition to describe $f(L, t)$ demonstrates that both solutions are mass conserving.

The use of a Danckwerts-type boundary condition at the interface in equation (11) implicitly assumes that there is no dispersion in the second layer. In reality, there will be some dispersion in the exit apparatus. Imposing continuity in resident concentration at the interface and transforming to flux concentrations yields

$$\frac{v}{R} \cdot \frac{\partial C_f(L^-, t)}{\partial x} = \frac{v_e}{R_e} \cdot \frac{\partial C_f(L^+, t)}{\partial x} \quad (12)$$

Equation (12) in conjunction with continuity in flux concentrations at the interface forms a second-type boundary condition [Kreft, 1981; Leij, et al., 1991]. The solution in the Laplace domain for a semi-infinite second layer (5), inlet boundary condition (4), and initial condition (7) is [Kreft, 1981; Barry and Parker, 1987]

$$\bar{C}_f(x, s) = \frac{2\lambda \cdot (1 + \lambda_e) \cdot \exp \left(\frac{vL \cdot (1 - \lambda)}{2D} + \frac{v_e \cdot (x - L) \cdot (1 - \lambda_e)}{2D_e} \right)}{s \cdot (1 + \lambda) \cdot (\lambda + \lambda_e) - (1 - \lambda) \cdot (\lambda_e - \lambda) \cdot \exp \left(\frac{-\lambda vL}{D} \right)} \quad x > L \quad (13)$$

$$\lambda = \left(1 + \frac{4sRD}{v^2} \right)^{\frac{1}{2}} \quad \lambda_e = \left(1 + \frac{4sR_e D_e}{v_e^2} \right)^{\frac{1}{2}}$$

where s is the Laplace transform variable. Inspection of the solution for the first layer [e.g. Leij, et al., 1991; Leij and van Genuchten, 1995] shows that the properties of the second layer influence the concentration profile in the first layer. Unlike equation (11), (13) implies that layer ordering will influence effluent concentrations.

3. Materials and Methods

Undisturbed soil columns were collected from a study site in southern Costa Rica. The soil is a fine textured Ultisol (clayey kaolinitic semiactive isohyperthermic Oxyaquic Hapludult) derived from sedimentary rocks rich in mafic materials. The bulk density of the soil ranged from 0.8 Mg m⁻³ at the surface to approximately 1.1 Mg m⁻³ in the subsoil. Columns of soil samples were collected at 0 to 15 cm, 20 to 40 cm, and 42 to 57 cm depths corresponding to the Ap/AB, Bt1, and Bt2 horizons, respectively. A total of eight columns were collected for this study: three from each of the Ap/AB and Bt1 horizons and two from the Bt2 horizon. Cylindrical soil columns (10.1 cm i.d.) were isolated by incrementally forcing a beveled cutting edge coupled to a polyvinyl chloride pipe over a previously carved pedestal of soil. The interior of the cutting edge and pipe were coated with petroleum jelly to

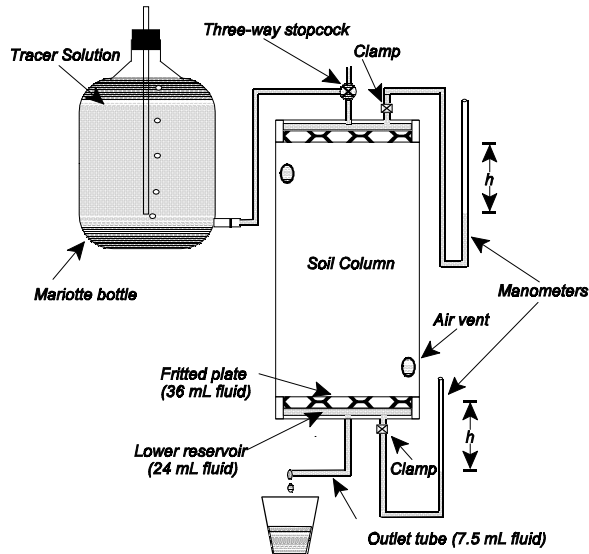


Figure 2. Schematic diagram of the column and associated flow apparatus.

facilitate lubrication [Seyfried and Rao, 1987; Cook *et al.*, 1993]. Excess soil material at the bottom and top of the cylinders was trimmed flush. The soil was well aggregated and only a small amount of smearing resulted from the trimming procedure.

The bottom and top of each column were fitted with fritted glass plates 6 mm thick (see Figure 2) with bubbling pressure heads ranging from -3.9 to -5.1 kPa. Contact between fritted glass plates and the soil was facilitated by placing a small amount of uniform fine-grade (#60 sieve) sand between the plate and the rough surface of the soil. Soil columns were slowly saturated with 5.0 mM CaCl_2 from the bottom porous plate prior to affixing the top plate assembly and initiating a set

of displacement experiments. The inlet pressure head was controlled with a Mariotte device and the outlet pressure head was maintained by adjusting the elevation of the outflow tube. Once columns were saturated, displacement experiments were conducted under a unit hydraulic gradient at selected pressure heads using 5.0 mM CaBr_2 as the influent solution. Displacement experiments used to evaluate the adequacy of formulated boundary conditions were conducted at -10, -11, or 14 cm of pressure head. Displacement experiments used to evaluate the effect of boundary disturbances were conducted at -5 cm or -7.5 of pressure head (Table 1). The bromide tracer was injected continuously only after a steady state flux of 5.0 mM CaCl_2 had been established. Significant effluent mixing with dead volume of the lower manometer was avoided by clamping the access tube at the initiation of the displacement experiments. Flushing out the upper reservoir at the initiation of experiments [e.g. Seyfried and Rao, 1987 and Jardine *et al.*, 1993] was not possible as this caused a partial desaturation of the soil and a consequent decrease in flow rates. As an alternative, the upper manometer was clamped, rinsed and refilled with tracer solution immediately after the initiation of each displacement experiment. Influent solution containing the Br^- tracer was continued for approximately five pore volumes or until effluent tracer concentrations were approximately greater than 95% of the influent concentration. Only a single displacement experiment was completed for columns 5, 6, 8 and 11 whereas a total of three displacements were completed for columns 1 through 4 (Table 1). Once a given breakthrough run was completed for a specified head, columns 1 through 4 were again flushed with 5.0 mM CaCl_2 solution to displace the tracer in the soil. During these displacements, the column was saturated several times to ensure the equilibration of concentration throughout all pores. The succeeding breakthrough run at the next lowest head was initiated when effluent CaBr_2 concentrations were approximately less than 5 μM .

Table 1. Physical Parameters for Column Displacement Experiments

Column ^a	Horizon	Pressure head cm H ₂ O	θ cm ³ cm ⁻³	θ_{sat}^b cm ³ cm ⁻³	L cm	$v \cdot \theta^c$ cm h ⁻¹	Pe^d	Inlet apparatus
<i>Adequacy of Formulated Boundary Conditions</i>								
1	Ap/AB	-10.0	0.510	0.618	15.0	0.63	7.51	Plate
2	Ap/AB	-10.0	0.497	0.624	15.0	0.67	5.65	Plate
3	Bt1	-10.0	0.514	0.656	20.0	1.47	10.04	Plate
4	Ap/AB	-11.0	0.636	0.680	14.9	1.11	4.59	Plate
5	Bt2	-10.0	0.547	0.588	14.9	0.82	7.39	Plate
6	Bt1	-10.0	0.554	0.610	20.0	2.17	2.52	Plate
8	Bt2	-10.0	0.568	0.573	14.9	1.58	1.91	Plate
11	Bt1	-14.0	0.618	0.636	20.0	1.17	2.73	Plate
<i>Evaluation of Inlet Boundary Disturbances</i>								
1	Ap/AB	-5.0	0.538	0.618	15.0	4.34	4.25	Plate
1	Ap/AB	-5.0	0.538	0.618	15.0	4.36	3.78	Drip
2	Ap/AB	-5.0	0.527	0.624	15.0	4.91	4.55	Plate
2	Ap/AB	-5.0	0.527	0.624	15.0	5.03	4.75	Drip
3	Bt1	-5.0	0.535	0.656	20.0	5.58	6.09	Plate
3	Bt1	-5.0	0.535	0.656	20.0	5.40	5.91	Drip
4	Ap/AB	-7.5	0.659	0.680	14.9	5.64	3.46	Plate
4	Ap/AB	-7.5	0.659	0.680	14.9	5.65	3.90	Drip

^aNumbers signify different columns.

^bVolumetric water content of media at saturation.

^cVolumetric flux.

^dNonlinear least square fit of equation (8) to displacement experiments.

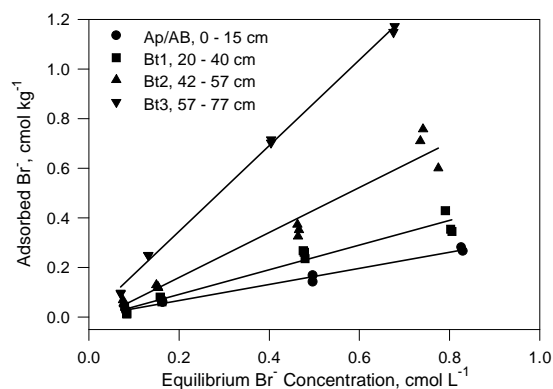


Figure 3. Batch adsorption isotherms of bromide for several horizons. Each point for a given horizon represents a repeated measurement. Lines represent the least squares fit of the linear isotherm to the data.

Upon the completion of all displacements using the upper fritted plate assembly, columns 1 through 4 were saturated with 5.0 mM CaCl_2 and again subjected to a pressure head of -5 or -7.5 cm H_2O (0.49 or 0.74 kPa). Once steady state flux had been achieved at this pressure head, the top fritted plate assembly was removed to allow the flux controlled application of tracer solution using a drip applicator (an acrylic reservoir fitted with 34 (30 gauge) dispensing tips). Four displacement experiments (columns 1 through 4) were conducted using the drip applicator to apply influent solution of 5.0 mM CaBr_2 to the soil surface (Table 1). The flow rate of the drip applicator was adjusted to match the mean flux rate obtained with the fritted plate apparatus at -5 or -7.5 cm H_2O .

A final displacement experiment was conducted to quantify the degree of dispersion generated by the outlet apparatus. Influent 5.0 mM CaBr_2 was applied with 34 dispensing tips (32 gauge) to the surface of the porous plate and associated apparatus previously filled with 5.0 mM CaCl_2 . A small volume of solution (4 mL) was maintained on the surface of the porous plate to ensure that the entire plate was wetted. Effluent was collected from the outlet tube which was elevated to a height that maintained the small volume of solution at the surface of the plate. The flow rate of this displacement was $136 \text{ cm}^3 \text{ h}^{-1}$ which is of similar magnitude to flux rates through the soil columns at -10 cm H_2O (-0.98 kPa) pressure head.

Effluent from the column displacement experiments was collected over uniform time intervals corresponding to 0.1 to 0.15 pore volumes. Bromide concentrations in the effluent solution were measured using an ion-selective electrode. The ionic strengths of CaBr_2 standards were adjusted with CaCl_2 to 0.015 to match the ionic strength of the effluent exiting the columns. The soil columns were weighed at saturation and upon the completion of each displacement experiment. In addition, the oven dry weight of the soil in each column was measured after the completion of all transport studies. These measurements permitted the determination of the volumetric water content at saturation and at each pressure head (Table 1).

The physical parameters for each displacement experiment are shown in Table 1. Experiments examined for the adequacy

of formulated boundary conditions were limited to displacements at pressure heads of -10 cm of H_2O (-0.98 kPa) or less to avoid local nonequilibrium of adsorbed solute with solution concentrations exhibited at higher mean pore water velocities [Schwartz, 1998]. The evaluation of inlet boundary disturbances was limited to displacement experiments conducted at slightly higher flow rates to insure a more uniform areal flux distribution by the drip apparatus.

Dimensionless effluent concentrations $[C_f(L,t) - C_f(L,0)] / [C_0 - C_f(L,0)]$ were fitted to equations (8), (9) and (11) using an adaptive, model-trust region method of nonlinear, least-squares parameter optimization [Dennis *et al.*, 1981; Dennis and Schnabel, 1983]. Convergence problems and local minima were not detected for the minimization problems of this study. The series solution in (9) was obtained by summing the first 64 terms from smallest to largest values. For the column Péclet numbers of this study, the sixty-fourth term was always less than the current summation multiplied by the double precision machine accuracy ($2.2 \cdot 10^{-16}$). Where required, numerical derivatives of the analytical solution (9) were obtained by Richardson extrapolation [Ridders, 1982]. The integral in equation (11) was evaluated using an adaptive eight-point Legendre-Gauss algorithm. The Laplace transform equation (13) was numerically inverted using the modification of Weeks' method due to Garbow [1988]. Measured effluent concentrations were fitted to the one-layer ADE using L as the column length. For two layer models the distance from the inlet to the exit boundary, L_e , is set equal to $L + [4 \cdot V_e / (\theta_e \cdot \pi \cdot d^2)]$ where V_e is the volume of water contained in the exit apparatus and d is the column diameter (see Figure 2).

Batch methods were used to obtain Br^- adsorption isotherms of air dry, two mm sieve soil samples collected immediately adjacent to locations where the columns were collected. Six grams of soil were washed three times with 5 mM CaCl_2 to saturate the exchange complex with Ca^{2+} and Cl^- . After the final washing the supernatant was decanted and 30 mL of CaBr_2 solution at concentrations of 5, 3, 1 and 0.5 mmol L^{-1} (i.e. 10, 6, 2, and 1 mmol L^{-1} of Br^-) was added to the washed soil. The ionic strength of these solutions were maintained at 0.015 using CaCl_2 . These suspensions were mixed and allowed to equilibrate for 20 hours at 20 °C. After the designated time period, the suspension was centrifuged to collect the supernatant. Bromide concentrations were measured using an ion specific electrode. Adsorbed concentrations were calculated by subtracting the moles of Br^- measured in the equilibrium solution from the moles of each respective anion initially added.

4. Results and Discussion

4.1 Bromide Adsorption

Isotherms obtained from batch adsorption experiments with bromide (Figure 3) were linear within the range of equilibrium concentrations obtained (0.05 to 0.9 cmol L^{-1} Br^-). A close similarity of Br^- adsorption with Br^- desorption breakthrough curves in binary systems with Cl^- for these soils [Schwartz, 1998] provide further evidence that isotherms are approximately linear. The small amount of positive charge likely results from the presence of goethite, which ranges from

Table 2. Comparison of Parameters Obtained by Fitting the Semi-Infinite and Finite Solutions to Measured Concentrations

Column ^a	Semi-infinite solution, Equation (8)				Finite solution Equation (9)		
	v cm h ⁻¹	D cm ² h ⁻¹	R	RSD ^b × 10 ⁻²	D cm ² h ⁻¹	R	RSD ^b × 10 ⁻²
1	1.23	2.45	1.50	1.09	2.86	1.50	1.16
2	1.34	3.57	1.57	0.75	4.45	1.57	0.66
3	2.87	5.71	2.00	0.63	6.38	2.00	0.66
4	1.75	5.68	1.16	0.98	7.45	1.16	1.16
5	1.49	3.01	3.04	0.69	3.52	3.03	0.77
6	3.93	31.1	1.53	0.96	56.5	1.48	1.08
8	2.79	21.7	2.89	0.72	45.1	2.70	0.97
11	1.89	13.8	1.40	1.05	21.6	1.35	1.45

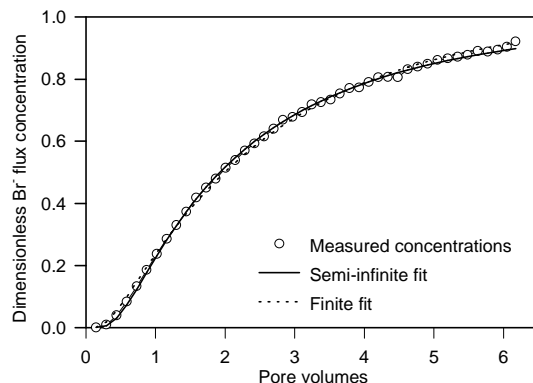
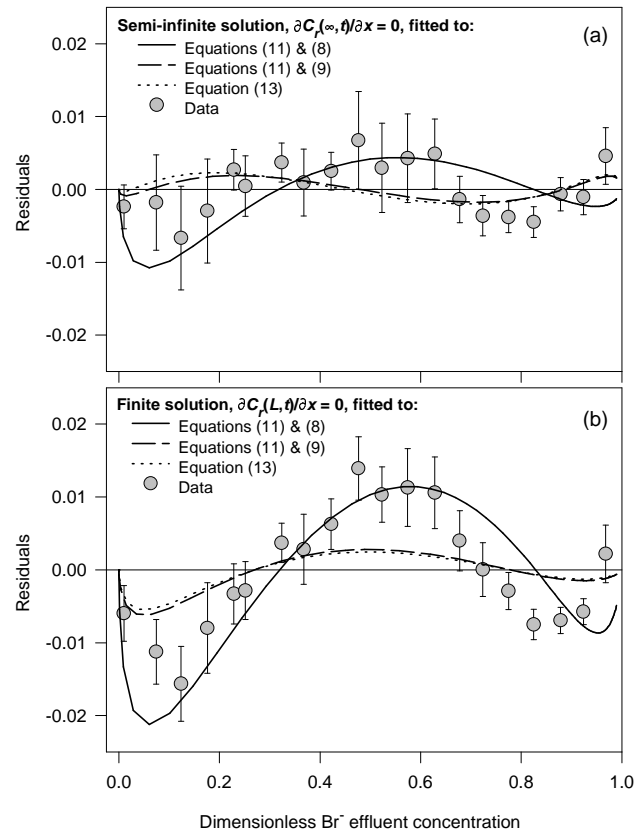
^aNumbers signify different columns.^bResidual standard deviation

7 to 11 percent in these soils, and an equilibrium pH in batch solutions and column effluent of approximately 4.6 [Schwartz, 1998]. Since equilibrium adsorption isotherms of bromide are linear within the concentration range used in the displacement experiments of this study, the use of retardation factors in equation (1) is justified.

4.2 Exit Boundary Conditions

The parameters obtained from the nonlinear least-squares fit of equations (8) and (9) to measured concentrations are shown in Table 2. (For convenience, equations (8) and (9) are hereafter designated as the “semi-infinite” and “finite” analytical solutions, respectively.) The finite analytical solution consistently predicted a larger dispersion coefficient than the semi-infinite solution (Table 2). Despite these differences, predicted effluent concentration curves of the two analytical models agreed closely (Figure 4). The retardation factor was not significantly ($p = 0.149$, $n = 8$) influenced by the type of boundary used. This supports the assertion by *van Genuchten and Parker* [1984; 1985] that both solutions can be used to derive adsorption or exchange coefficients from column displacement experiments.

Figures 5a and 5b provide a summary of the deviations of the dimensionless concentrations measured in the effluent from the semi-infinite and finite one-layer analytical solutions, respectively. The deviations between measured and predicted concentrations, termed residuals (i.e. measured minus

**Figure 4.** Observed Br⁻ effluent concentrations for column 8 at -10 cm H₂O pressure head and the corresponding fitted finite and semi-infinite solutions.**Figure 5.** Variation of residuals across concentrations for the semi-infinite (a) and finite (b) analytical solutions. Points and error bars are mean and 95% confidence intervals of residuals, respectively, for a given concentration range. Lines show residuals predicted by fitting the semi-infinite and finite solutions to two-layer simulations with $v = 3.0$ cm h⁻¹, $\theta = 0.57$, $D = 15$ cm h⁻¹, $R = 2.0$, $L = 15.0$ cm, $L_e = 16.35$ cm, $\theta_e = 0.56$, $D_e = 0.56$ cm h⁻¹, and $R_e = 1.0$.

predicted concentrations), are used herein to assess the degree of discrepancy between the assumed boundary conditions for each model and the observed data. The finite analytical solution had larger absolute values of residuals than the semi-infinite solution over nearly all concentration ranges (symbols

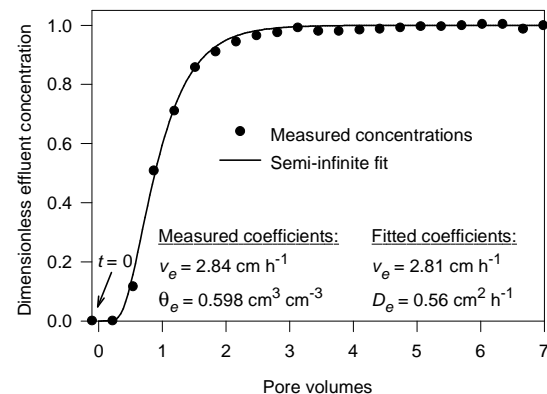
**Figure 6.** Displacement results for the column apparatus and fitted semi-infinite solution. The pore volumes corresponding to measured concentrations have been adjusted to reflect the travel time in the outlet tube (see Figure 2).

Table 3. Comparison of Parameters Obtained by Fitting the Semi-infinite Solution to Measured Effluent Concentrations for Plate and Drip Apparatus Inlet Conditions

Column	Plate apparatus				Drip apparatus			
	v cm h^{-1}	D $\text{cm}^2 \text{h}^{-1}$	R	RSD ^a $\times 10^{-2}$	v cm h^{-1}	D $\text{cm}^2 \text{h}^{-1}$	R	RSD ^a $\times 10^{-2}$
1	8.07	28.5 (± 0.573)	1.41 (± 0.006)	0.81	8.11	32.2 (± 0.896)	1.32 (± 0.008)	1.08
2	9.33	30.7 (± 0.832)	1.52 (± 0.009)	1.05	9.55	30.1 (± 0.410)	1.50 (± 0.004)	0.52
3	10.4	34.3 (± 0.340)	2.02 (± 0.004)	0.48	10.1	34.2 (± 0.350)	1.95 (± 0.004)	0.49
4	8.55	36.8 (± 0.535)	1.09 (± 0.004)	0.57	8.56	32.8 (± 0.415)	1.13 (± 0.003)	0.50

Asymptotic standard errors are shown in parentheses.

^aRSD, Residual standard deviation.

in Figure 5a and 5b) and consequently larger residual standard deviations (RSD) than the semi-infinite solution (Table 2). (Here RSD is equivalent to the sum of squared residuals divided by the model degrees of freedom.) The systematic trend in residuals shown in Figure 5 was characteristic of both analytical solutions. Part of the departure of measured effluent concentrations from the ADE may have been caused by a small amount of physical nonequilibrium which was confirmed for these columns at higher pore water velocities [Schwartz, 1998]. In any case, a portion of the deviation of predicted concentrations from measured concentrations is caused by the failure of equations (8) and (9) to include the effects generated by the outlet apparatus. The hypothetical influence of the outlet apparatus upon measured concentrations can be generated using a two-layer transport equation given by (11) or (13). This is accomplished by 1) simulating exit concentrations at the outlet (L_e) using either (11) or (13) and 2) fitting equations (8) and (9) to these simulated concentrations to obtain residuals. Displacement results shown in Figure 6 indicate that the degree of dispersion generated by the outlet apparatus is moderate at a pore water velocity of 2.9 cm h^{-1} . Accordingly, a dispersion coefficient D_e of $0.56 \text{ cm}^2 \text{h}^{-1}$ and a mean pore water velocity of 3.0 cm h^{-1} were used to simulate concentrations in the second layer representing the outlet apparatus. Dispersion through the outlet tube (Figure 2) was assumed to be negligible. Hence the calculated travel time through the tube (0.055 hours for $v=3.0 \text{ cm h}^{-1}$) was added to the times corresponding to the simulated concentrations in Figure 5.

The residuals predicted by fitting the semi-infinite and finite solutions to two-layer simulations (i.e. simulated two-layer concentrations minus predicted concentrations from a one-layer fit) are shown in Figures 5a and 5b, respectively. Although the residuals predicted by fitting either the semi-infinite solution or finite solution to two-layer simulations largely fall within the 95% confidence intervals of the actual residuals, equation (11) with $f(L,t)$ given by (8) best reproduces the systematic positive and negative trends exhibited by the data. The close agreement between equations (13) and (11) with $f(L,t)$ given by (9) is expected since dispersion in the outlet apparatus is small relative to the dispersion in the porous media. Although the effects of the inlet apparatus were not included in the simulations shown in Figure 5, inclusion of such effects in this analysis would only

magnify the positive and negative oscillations exhibited by the residuals simulated in Figure 5. These results suggest that equation (11) with the interface flux given by (8) best describes the effluent concentrations at the outlet. This implies that the resident concentrations at the interface between the soil and porous plate are discontinuous, at least in a macroscopic sense. Novakowski [1992b] also found that the solution which forced discontinuities in resident concentrations at the interface between the outlet reservoir and the porous media provided a better fit to the experimental data. Comparison of dispersion coefficients in Table 2 with the molecular diffusion of $0.075 \text{ cm}^2 \text{h}^{-1}$ for Br⁻ in water [Robinson and Stokes, 1959] indicates that the apparent dispersion produced at these mean velocities for these soil columns was largely (>97%) controlled by variations in axial velocity. Hence, the better fit provided by the semi-infinite solution supports van Genuchten and Parkers' [1985] rationalization that solute distributions inside the finite column should be unaffected by the presence of an outflow boundary when dispersion is governed principally by advection.

4.3 Inlet and Outlet Boundary Disturbances

Dispersion coefficients and retardation factors obtained by fitting (8) to effluent concentrations from columns with platen and drip-type inlet apparatus are shown in Table 3. There was obviously a close similarity between effluent concentrations obtained using either inlet device (Figures 7 and 8). Paired comparisons of fitted parameters obtained with porous plate

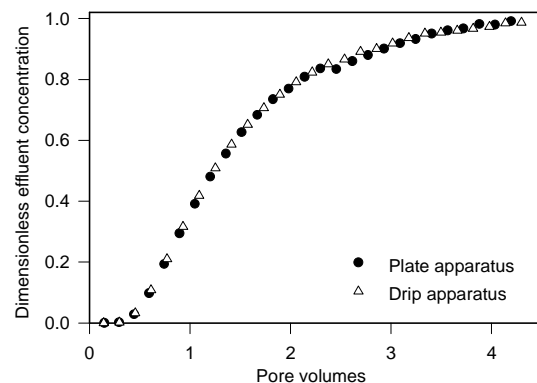


Figure 7. Observed Br⁻ effluent concentrations for column 2 using the fritted glass plate apparatus and the drip application method.

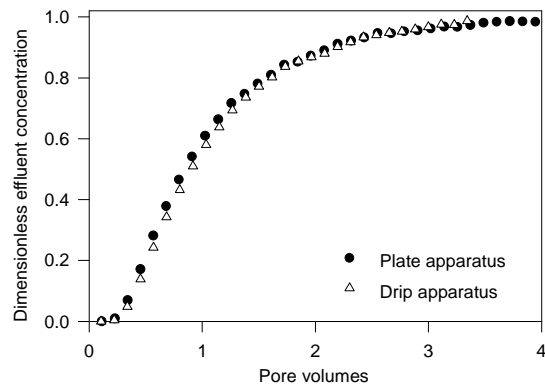


Figure 8. Observed Br^- effluent concentration for column 4 using the fritted glass plate apparatus and the drip application method.

and drip apparatus yielded no significant difference for the dispersion coefficient ($p = 0.884$; $n = 4$) and the retardation factor ($p = 0.314$; $n = 4$).

Equation (11) in conjunction with (8) is used to interpret the experimental data and investigate the influence of the inlet and outlet apparatus upon effluent concentrations. The influence of the outlet apparatus upon the effluent concentrations is first considered without including the effects of the inlet apparatus. The effects of both the inlet and outlet will be addressed subsequently. Equation (11) with the third-type interface boundary $f(L, t)$ described by the semi-infinite solution (8) was fitted to observed concentrations using nonlinear least squares regression. For this analysis, the dispersion coefficient of the outlet apparatus is assumed to be proportional to velocity such that D_e/v_e is constant and equivalent to the ratio obtained from the breakthrough curve in Figure 6. These fits yielded a reduction in the residual standard deviation relative to the one-layer semi-infinite equation in ten out of the sixteen cases shown in Tables 2 and 3. This is an important result since, in theory, a lower residual standard deviation cannot be obtained by fitting a one-layer model (8) to two-layer system simply by setting L equal to L_e . The dispersion coefficients obtained from the one-layer semi-infinite solution fit in Tables 2 and 3 are underestimated by about 14 percent when the effect of the outlet apparatus was considered (Figure 9a). In contrast, *James and Rubin* [1972] found that the dispersions coefficient obtained from the one-layer treatment were 24 to 67 percent greater than the dispersion coefficient obtained from the two-layer treatment. The discrepancy between these studies is due to the low dispersivity and hence particularly large Péclet numbers ($63 < Pe < 387$) obtained for the glass bead columns used by *James and Rubin* [1972]. The direction and degree of the deviation of the fitted one-layer dispersion coefficient from the fitted two-layer dispersion coefficient essentially depends upon the values of the coefficients in equations (8) and (11). For column apparatus similar to that used in this study and for relatively dispersive media such that the column Pe is less than or equal to the exit apparatus Pe , the dispersion coefficient obtained from fitting the one-layer semi-infinite solution will underestimate the dispersion

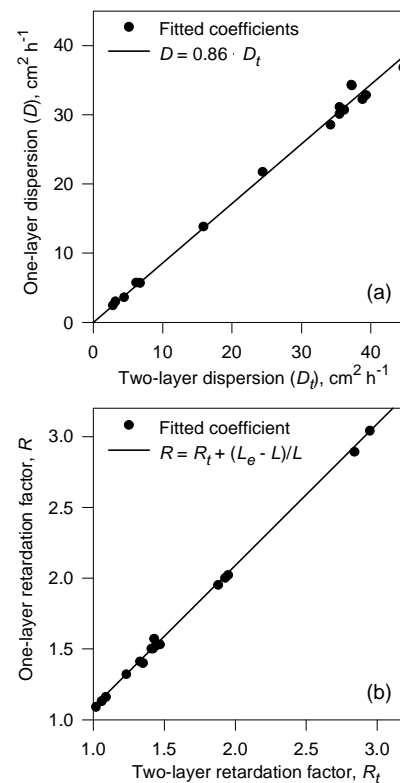


Figure 9. Comparison of the (a) dispersion coefficients and (b) retardation factors obtained by fitting one (equation (8)) and two-layer (equation (11) with (8)) models to measured effluent concentrations.

estimated from a two-layer treatment. Figure 9b demonstrates that the retardation factors are overestimated by no more than the fractional increase in pore volume imparted by the outlet apparatus (i.e. $L_e/L - 1$ when $\theta_e = \theta$). The linear response exhibited by the correlations of one and two-layer fitted coefficients in Figures 9a and 9b is a result of forcing D_e/v_e to be constant in conjunction with a nearly linear variation in D with respect to v for the soil horizons investigated.

The above results appear to contradict the preceding findings that indicate that the presence of the inlet apparatus has no effect upon the estimation of the dispersion coefficient and retardation factor. Recalling that layer ordering has no influence upon effluent concentrations predicted by (11), both the outlet and inlet apparatus can be treated as a single layer provided that they have identical dispersion coefficients. Under these conditions, the inlet apparatus would have nearly identical effect upon the effluent concentrations as the outlet apparatus. Yet inspection of Table 3 demonstrates that displacements conducted on columns with and without the inlet porous plate apparatus exhibited essentially the same degree of dispersion. Lack of a significant difference between porous plate and drip apparatus may be a result of an insufficient number of displacement experiments to detect any real differences. These results may also be a consequence of 1) a less uniform distribution of solution onto the soil surface by the drip apparatus and/or 2) a large dispersion coefficient for the porous plate apparatus at the inlet due to bypass flow.

Starr and Parlange [1977] found such flow irregularities generated at the inlet boundary to increase the apparent dispersion and hence tailing at the outlet. Flow irregularities within the inlet reservoir may induce a different effect. The relatively high velocity stream entering the reservoir could be transferred rapidly through the plate thereby bypassing a portion of the more stagnant reservoir and increasing the apparent dispersion within the apparatus. A large dispersivity for the inlet apparatus would in turn nearly negate its' influence upon effluent concentrations at the outlet. This is demonstrated by noting that as $D \rightarrow \infty$ and hence the interface flux concentration $f(L, t) \rightarrow 1$ for $t > 0$, $C_f(x, t)/C_0$ in equation (11) approaches $C_f(x, t)/C_0$ in equation (8).

The determination of the influence of both inlet and outlet upon fitted parameters is not feasible without a knowledge of the dispersion in the upper porous plate assembly. With the assumption that inlet and outlet dispersion is equivalent and $L_e = L + 2.7$ cm, the least-squares fit of equation (11) with $f(L, t)$ given by (8) to effluent concentrations suggests that the dispersion coefficients in Tables 2 and 3 (porous plate only) are underestimated by about 27%. If dispersion in the upper porous plate assembly is larger than the outlet apparatus, the underestimation of D more likely ranges from 14 to 27%. Consistent with the two-layer analyses of the outlet apparatus, inclusion of the inlet apparatus in the two-layer fits suggests that retardation factors in Tables 2 and 3 (porous plate only) are overestimated by no more than $[(L_e + L_i)/L] - 1$ where L_i is the effective length of the column inlet apparatus.

5. Conclusions

Experimental and simulated results were presented to evaluate the suitability of several possible solutions of the advective-dispersive equation to describe reactive solute transport in soil columns. The analytical solutions differed in the manner in which the interface boundary between the soil and the lower porous plate was described. Finite and semi-infinite solutions were observed to provide substantially different estimates of the dispersion coefficient. The deviation in simulated from measured effluent concentrations indicates that a semi-infinite interface boundary best approximates solute transport for columns at Péclet numbers ranging from 2 to 10. This solution corresponds to a continuous flux concentration and a macroscopically discontinuous resident concentration at the interface. Under the conditions of this study, diffusion of Br⁻ can account for no more than 3% of the apparent dispersion and hence little back mixing should be expected across the interface boundary. Since under a forward advection dominated system it is physically impossible to know concentrations or solute fluxes at downstream locations or outflow boundaries at future times, it seems appropriate that boundaries should be remote and far removed from any solute mass. An equivalent boundary naturally arises from a random walk of particles with a fixed forward velocity and random longitudinal displacements.

The influence of the inlet and outlet apparatus upon effluent concentrations and predicted least-squares parameters was also investigated. Modifications in the manner in which solute entered the soil boundary generated by the platen type inlet

apparatus and an array of dispensing tips that produced droplets at approximately the same fluxes were insufficient to significantly alter the observed effluent concentrations and fitted parameters. Failure to include the outlet and inlet disturbance created by porous plates in the analysis of effluent curves caused the dispersion coefficient to be underestimated by 14 to 27% for the conditions of this study. In addition, the retardation factor was overestimated by no more than the fractional increase in pore volume imparted by the platen apparatus. When precise estimates of parameters are required, the two-layer solution described by equation (11) with the interface flux concentration given by one-layer semi-infinite solution (8) should be utilized to estimate parameters provided that an estimate the dispersion generated by the outlet apparatus is available.

Notation

C_0	solute concentration in the entrance reservoir, ML^{-3} .
C_f	flux concentration, ML^{-3} .
C_r	resident concentration, ML^{-3} .
d	column diameter, L.
D	longitudinal dispersion coefficient of the porous media, $\text{L}^2 \text{T}^{-1}$.
D_e	dispersion coefficient of the exit apparatus, $\text{L}^2 \text{T}^{-1}$.
D_i	longitudinal dispersion coefficient of the porous media using two-layer treatment, $\text{L}^2 \text{T}^{-1}$.
L	column length, L.
L_e	effective length of exit apparatus plus column length, L.
L_i	effective length of inlet apparatus, L.
n	number of observations
p	p -value, probability of wrongly rejecting the null hypothesis if it is in fact true.
Pe	column Péclet number, $Pe = vL/D$.
R	retardation factor of the porous media.
R_e	retardation factor of the outlet apparatus.
t	time, T.
v	mean pore water velocity, L T^{-1} .
v_e	mean velocity of water in exit apparatus, L T^{-1} .
V_e	void volume of exit apparatus, L^3 .
x	distance from inlet, L.
θ	volumetric water content of the porous media, $\text{L}^3 \text{L}^{-3}$.
θ_e	volumetric water content of the porous media, $\text{L}^3 \text{L}^{-3}$.

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